Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

SUPPORTING INFORMATION FOR

Iron–catalyzed hydrosilylation of CO_2: CO_2 conversion to formamides and methylamines

*Xavier Frogneux, Olivier Jacquet and Thibault Cantat**

CEA, IRAMIS, SIS2M, F-91191 Gif-sur-Yvette France.

CNRS, UMR SIS2M n° 3299 CEA – CNRS, F-91191 Gif-sur-Yvette France.

E-mail: thibault.cantat@cea.fr

Experimental details

General considerations

All reactions and manipulations were performed at 20 ºC in a recirculating mBraun LabMaster DP inert atmosphere (Ar) drybox and vacuum Schlenk lines. Glassware was dried overnight at 60 ºC before use. All NMR spectra were obtained using a Bruker DPX 200 MHz spectrometer. Chemical shifts for ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced to solvent impurities. Mass spectrometer data were collected on a Shimadzu GCMS-QP2010 Ultra gas chromatograph mass spectrometer equipped with a Supelco SLB^{TM}-ms fused silica capillary column (30 m x 0.25 mm x 0.25 µm). Unless otherwise noted, reagents were purchased from commercial suppliers and dried over 4 Å molecular sieves prior to use. Celite (Aldrich), alumina (Brockman I, Aldrich) and 4 Å molecular sieves (Aldrich) were dried under dynamic vacuum at 250 °C for 48 h prior to use. Tetrahydrofuran (THF), 1,4-dioxane and toluene were dried over a sodium(0)/benzophenone mixture and distilled before use. Acetonitrile, dichloromethane were dried over CaH_2 and distilled before use. $Fe(acac)_2$ was purchased from Sigma-Aldrich with 99.95 % trace metal basis. Carbon dioxide was purchased from Messer in a 5.5 purity gas bottle.

Typical procedure for the catalytic formylation of amines to formamides:

The typical procedure is detailed for the conversion of *N*-methylaniline (**1a**) to *N*-methylformanilide (**2a**) using {$Fe(acac)_2$ + PP_3} as catalyst. Under inert atmosphere (Ar), A 16 mL J. Young Schlenk flask, equipped with a magnetic stir bar and a J. Young valve, is charged successively with a solution of $Fe(acac)_2$ (3.2 mg, 0.0125 mmol) and PP_3 (8.4 mg, 0.0125 mmol) in 0.7 mL of anhydrous THF, *N*-methylaniline (**1a**) (27 µL, 0.250 mmol), and phenylsilane (31.0 µL, 0.250 mmol). The reaction mixture is exposed to a CO_2 atmosphere (1 bar) and the flask is sealed and stirred vigorously at RT for 18 h. The corresponding *N*-

methylformanilide (**2a**) is identified and the yield and conversion were determined by ^{1}H NMR in $CDCl_3$ and GC/MS using mesitylene as an internal standard, after calibration.

Procedure for the isolation of **2a**: the crude mixture is quenched with ethyl acetate (5 mL), filtered through Celite, concentrated under vacuo and purified by flash chromatography on silica gel (0.069-0.200 mm), standard grade using *n*-pentane:ethyl acetate (80:20) as the eluent. After removal of the solvent under reduced pressure, this method afforded analytically pure **2a** as colorless oil. Average isolated yield over two runs: 92 %, 62.2 mg.

Typical procedure for the catalytic methylation of amines:

The typical procedure is detailed for the conversion of *N*-methylaniline (**1a**) to *N*-methylformanilide (**2a**) using {$Fe(acac)_2$ + PP_3} as catalyst. Under inert atmosphere (Ar), A 16 mL J. Young Schlenk flask, equipped with a magnetic stir bar and a J. Young valve, is charged successively with a solution of $Fe(acac)_2$ (1.6 mg) and PP_3 (4.2 mg) in 0.35 mL of anhydrous THF, *N*-methylaniline (**1a**) (13.5 μL, 0.125 mmol), and phenylsilane (62.0 μL, 0.5 mmol). The reaction mixture is exposed to a CO_2 atmosphere (1 bar) and the flask is sealed and stirred vigorously in an oil bath at 100 °C for 18 h. The corresponding *N,N*-dimethylaniline (**2a**) is identified and the yield and conversion were determined by ^{1}H NMR in $CDCl_3$ and GC/MS using mesitylene as an internal standard, after calibration.

Iron-catalyzed hydrosilylation of 2a to 3a:

Under inert atmosphere (Ar), A 16 mL J. Young Schlenk flask, equipped with a magnetic stir bar and a J. Young valve, is charged successively with a solution of $Fe(acac)_2$ (3.2 mg) and PP_3 (8.4 mg) in 1 mL of anhydrous THF, *N*-methylformanilide (**2a**) (31 μL, 0.250 mmol), and phenylsilane (31 μL, 0.250 mmol). The flask is sealed and stirred vigorously in an oil bath at 100 °C for 22 h. The corresponding *N,N*-dimethylaniline (**3a**) is identified and the yield and conversion were determined by ^{1}H NMR in $CDCl_3$ and GC/MS using mesitylene as an internal standard, after calibration.

^{1}H NMR and **^{13}C NMR** of the following formylated products are identical to reported data: **2h**[1], **2l**[2], **2s**[3], **2t**[4], **3x**[5], **2m'**[6], **2o**[7], **2y**[8], **2x**[9].

^{1}H NMR and **^{13}C NMR** of the following products were compared with commercial samples purchased from Aldrich or Acros: **2a, 2b**, **2c**, **2d**, **2e**, **2i**, **2j**, **2k**, **2m**, **2n**, **2u**, **3a, 3y.**

Selected data for **2v**:

^{1}H NMR ($CDCl_3$) δ: 9.45 (d, *J* = 10Hz, 0.5 H), 8.99 (s, 1H), 8.85 (d, *J* = 10 Hz, 0.5H), 8.40 (s, 1H), 7.85-8.06 (m, 4H), 7.65 (d, *J* = 8 Hz, 2H), 7.15 (d, *J* = 8 Hz, 1H), 4.24 (t, 4H), 1.56-1.78 (m, 4H), 1.51-1.26 (m, 4H), 0.92 (t, 6H).

^{13}C NMR ($CDCl_3$) δ: 166.36, 166.14, 162.54, 159.94, 141.43, 141.25, 131.36, 130.71, 126.60, 126.08, 119.21, 117.12, 64.91, 30.65, 19.19, 13.70.

GC/MS: IE (m/z): 221 (M+, 12); 165 (100); 148 (80); 137 (35); 93 (100); 120 (52)

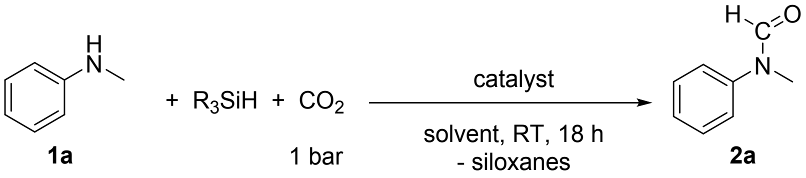
Selected data for **2r**:

^{1}H NMR ($CDCl_3$) δ: 13.25 (br, 1H), 8.30 (s, 0.6H), 7.92 (s, 0.4H), 3.37-2.62 (m, 8H), 2.53 (s, 3H).

^{13}C NMR ($CDCl_3$) δ: 165.58, 158.99, 54.60, 53.22, 43.97.

GC/MS: IE (m/z): 143 (M+, 7); 128 (3); 115 (5); 99 (100)

Complete table for the optimization of the iron-based catalytic system:



Entry[a]	Catalyst (mol%)	Solvent	Hydrosilane (eq)	Conversion[b] (%)
1	$Fe(acac)_2$ (5.0) + PP_3 (5.0)	THF	$PhSiH_3$ (1)	> 95
2	$Fe(acac)_2$ (5.0)	THF	$PhSiH_3$ (1)	<1
3	PP_3 (5.0)	THF	$PhSiH_3$ (1)	<1
4	$Fe(acac)_2$ (5.0) + PPh_3 (20.0)	THF	$PhSiH_3$ (1)	<1
5	$Fe(acac)_2$ (5.0) + dppp (10.0)	THF	$PhSiH_3$ (1)	<1
6	$Fe(acac)_2$ (5.0) + dppf (10.0)	THF	$PhSiH_3$ (1)	<1
7	$Fe(acac)_2$ (5.0) + dppBz (10.0)	THF	$PhSiH_3$ (1)	<1
8	$Fe(acac)_2$ (5.0) + XantPhos (10.0)	THF	$PhSiH_3$ (1)	<1
9	$Fe(acac)_2$ (5.0) + tmeda (10.0)	THF	$PhSiH_3$ (1)	<1
10	$Fe(BF_4)_2.6H_2O$ (5.0) + PP_3 (5.0)	THF	$PhSiH_3$ (1)	13
11	$Fe(acac)_2$ (5.0) + PP_3 (5.0)	CH_3CN	$PhSiH_3$ (1)	> 95
12	$Fe(acac)_2$ (5.0) + PP_3 (5.0)	CH_2Cl_2	$PhSiH_3$ (1)	> 95
13	$Fe(acac)_2$ (5.0) + PP_3 (5.0)	toluene	$PhSiH_3$ (1)	63
14	$Fe(acac)_2$ (5.0) + PP_3 (5.0)	1,4-dioxane	$PhSiH_3$ (1)	48
15	$Fe(acac)_2$ (5.0) + PP_3 (5.0)	THF	Et_3SiH (3)	<1
16	$Fe(acac)_2$ (5.0) + PP_3 (5.0)	THF	$(EtO)_3SiH$ (3)	<1
17	$Fe(acac)_2$ (5.0) + PP_3 (5.0)	THF	Et_2SiH_2 (1.5)	<1
18	$Fe(acac)_2$ (5.0) + PP_3 (5.0)	THF	Ph_2SiH_2 (1.5)	<1
19	$Fe(acac)_2$ (5.0) + PP_3 (5.0)	THF	TMDS (3)	<1
20	$Fe(acac)_2$ (5.0) + PP_3 (5.0)	THF	PMHS (3)	<1[d]
21	$Fe(acac)_2$ (1) + PP_3 (1)	THF	$PhSiH_3$ (1)	28
22	$Fe(acac)_2$ (0.1) + PP_3 (0.1)	THF	$PhSiH_3$ (1)	<1

PP_3: tris[2-(diphenylphosphino)ethyl]phosphine
dppp: 1,3-bis(diphenylphosphino)propane
dppf: 1,1′-bis(diphenylphosphino)ferrocene
dppBz: 1,2-bis(diphenylphosphino)benzene
XantPhos: 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene
tmeda: *N,N,N′,N′*-tetramethylethylenediamine

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